OFFICE OF NAVAL RESEARCH

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TECHNICAL REPORT NO. 14

Semiclassical Description of Inelastic Atom Scattering by Surfaces

by

Walter Kohn

Department of Physics

University of California, Santa Barbara

Santa Barbara, CA 93106

Prepared for publication

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Semiclassical Description of Inelastic Atom Scattering by Surfaces

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Preface:

My friendship with Howard Reiss goes back over a little more than one-half of our lives, to the summer of 1953. I had come to Bell Labs on the first of about a dozen annual summer visits and found Howard in masterly command of the theory of solid solutions of Group III and Group V atoms (acceptors and donors) and their complexes in *Si* and *Ge*. This was, of course, during the heady years of the spectacular transistor revolution, and Howard's work was at the theoretical center of the preparation of the essential n- and p-doped samples of *Si* and *Ge*. As a neophyte in solid state physics I was enormously impressed (not to say intimidated) by the breadth of understanding and variety of techniques which Howard had at his command.

In the intervening years we both moved–along quite different paths–into faculty positions at the University of California, and there have been many occasions when I have enjoyed, and frequently profited from, Howard's extraordinary qualities as a scientist. His great originality and outstanding ability to solve, somehow, almost any reasonable problem in physical or solid-state chemistry are truly astonishing.

Howard is equally at home in classical and quantum theory. I hope, therefore, that the following contribution, which is on the borderline between classical and quantum physics (or chemistry) will be to his liking.

I. Introduction

In many branches of quantum physics a semi-classical description has been the most appropriate and most instructive. Two examples are: bound states in atoms and molecules, of high quantum numbers n; and the description of crystal electrons in a weak magnetic field H, where the large parameter is the label n of the Landau level (or, in complicated geometries, something similar). Semiclassical treatments of scattering of a particle by a fixed external potential are also long familiar and governed by the BWK equation or

semiclassical path integral methods.

The problem of inelastic scattering of an atom by a surface is conceptually and calculationally much more difficult. If the velocity of the incident atom ("incidon") is sufficiently smaller than typical electronic velocities–and this is true up to $\sim 1k\,eV$ for H and $\sim 100\,k\,eV$ for heavy atoms–the Born Oppenheimer approximation is valid and the system can be described by a Hamiltonian of the form

$$H = \frac{p^2}{2m} + \left(\sum_j \frac{p_j^2}{2M} + W(r_1, \cdots r_N) \right) + \sum V(r; r_1, \cdots r_N) \qquad (1)$$

where (m, p, r) describe the incidon, and (M, p_j, r_j) the N lattice atoms. Thus electronic degrees of freedom are completely represented by the interaction potentials W and V. We shall limit ourselves to this Born-Oppenheimer régime.

Provided that the surface temperature, T, is much greater than the Debye temperature θ_D and the incident atom has a DeBroglie wavelength much shorter than a characteristic length of the surface (say $<<10^{-8}\,cm$) a fully classical description evidently is in order. If these conditions are almost, but not quite, satisfied a semiclassical approach is clearly appropriate.

But what if, initially, the surface temperature $T$is smaller than the Debye temperature so that at least the high-lying modes are only weakly excited ($n = 0$ or 1) before the collision; or, a more extreme case, $T = 0$, so that initially all modes are in their $n = 0$ ground-states? Is the classical (normally $n>>1$) limit at all an appropriate starting point? And what are the appropriate conditions, if any, on the masses m and M, the incident velocity v, and other parameters such as interaction strengths and ranges?

A good deal of progress has been made in recent years on semiclassical inelastic scattering theory. It is of great interest not only for atom-surface scattering but also for scattering of molecules by surfaces, accompanied by internal molecular excitations, and, of course,

related to chemical reactions between gaseous molecules. To my mind, the above and other questions have not yet been fully answered and considerable work remains to be done.

1. A Simple Model and a Check on the Trajectory Approximation.

In recent work by our group we have critically examined a simple model in which the atoms of the surface are schematized as a single one-dimensional harmonic oscillator. Our Hamiltonian is

$$H = \frac{p^2}{2m} + \left(\frac{P^2}{2M} + \frac{K}{2} X^2 \right) + e^{-(X-x)/a} \tag{2}$$

By a simple change of variable, $x \rightarrow x + b$, we have set, without loss of generality, the interaction amplitude equal to unity. Similar models have been studied extensively in the past from various points of view.[1] Our objectives have been two-fold. (1.) We start with the harmonic oscillator in the ground state and calculate the energy loss spectrum of the incidon exactly up to and including the leading quantum mechanical correction ($0(h^{1/2})$). (2.) We compare these results with those of the so-called trajectory approximation[2] (which has semiclassical features) to determine under which conditions, if any, that approximation is valid.

In our model there are 2 dimensionless classical parameters: $\mu_1 \equiv m/M$, and $\mu_2 \equiv \omega\tau$, where ω is the frequency of the oscillator ($\omega = K^{1/2}M^{-1/2}$) and τ is the time taken by the incidon, of energy E, to traverse the distance a ($\tau = a\, m^{1/2}(2E)^{-1/2}$).

Our method of solution is to develop a singular limiting solution of the Heller wavepacket equations.[3] Heller's method starts with the oscillator in its Gaussian groundstate and the incidon described by a distant, incoming Gaussian wave packet of the form

$$\psi(x,t) = A \int dp e^{-(p-p_o)^2/h\alpha} e^{-\frac{i}{h}(p(x-x_o)+E(p)t)} \tag{3}$$

Here p_o and x_o are the initial mean momentum and position; $E(p) \equiv p^2/2m$; $(h\alpha)^{1/2}$ is the momentum width of the incident wave-packet; and A is the appropriate normalization constant.

The following heuristic argument suggests (correctly, as we have confirmed) that the momentum (and energy) distribution of the reflected particle will have a width $\propto h^{1/2}$ for $h \to 0$: The target oscillator has a zero-point momentum distribution of width $\Delta P \sim (h\omega M)^{1/2}$ which, using classical mechanics, leads to a distribution of reflection momenta of $\Delta p \sim \Delta P \propto h^{1/2}$. To distinguish this real quantum spread from the artificial momentum spread of the incident wave-packet we must make the latter relatively negligible, i.e.,

$$(h\alpha)^{1/2} << f(\mu_1 \mu_2)(h\omega M)^{1/2} \text{ or}$$

$$\alpha << (M\omega)^{1/2} \; f(\mu_1, \mu_2) \tag{4}$$

where f is some, as yet unknown, function of the dimensional parameters μ_1 and μ_2. Heller's equations become singular in the limit $\alpha \to 0$ and had to be solved with great care by an expansion in powers of α. The result is that, up to order $h^{1/2}$, the center of the reflected energy distribution is equal to the classical reflection energy; and that the width is given by

$$\Delta E = F(\mu_1, \mu_2)(h\omega)^{1/2}, \tag{5}$$

where $F(\mu_1, \mu_2)$ is a function of the dimensionless variables μ_1 and μ_2, which we have calculated for various values of μ_1 and μ_2 from our expansion of Heller's equations.

We have compared these results with those of the so-called trajectory approximation and, for any finite values of μ_1 and μ_2, find quantitative disagreements, from a few percent to factors of the order of 2. Thus we conclude that, while the trajectory approximation provides a useful orientation concerning the magnitude of quantum effects, it is not quantitatively correct.

2. Specific Quantum Effects in Atom Surface Scattering Experiments.

If an atom is incident on a perfect surface at temperature T with a definite momentum $\vec{p}_i$, its reflected momentum $\vec{p}_f$ will have a spread in both direction and magnitude.

Classically this spread is due to the different points of impact and to the different initial states of the target in the temperature ensemble. In addition, quantum mechanically, even for a given initial state of the target there are many possible final target states and corresponding final momenta $\vec{p}_f$. To isolate this last, specific quantum-mechanical effect we are proposing the following experiment: The target should be at temperature $T \approx 0$, so that variations of the initial target state are negligible. Secondly the reflected incidon is to be observed in a definite direction, θ_f. Classically one expects exactly 2 sharp reflection energies, $E_1(\theta_f), E_2(\theta_f)$ corresponding to precisely 2 inequivalent impact points leading to scattering in the chosen direction θ_f. (This effect is due to the warping of the surface.) If the quantum corrections are small each of these 2 sharp peaks will become a Gaussian line of finite width $\propto h^{1/2}$.

We are currently studying which surfaces, incident atom energies and directions of incidence promise to show this predicted quantum phenomenon most clearly.

Concluding Remarks.

Full accounts of this work will be published in the near future. I would like to acknowledge the collaboration of L. D. Chang in the work reported in Section 1 and discussions with K. Burke concerning Section 2. H. Metiu has introduced us to the Gaussian wavepacket techniques and on many occasions given us the benefit of his experience. D. N. Newns has acquainted us with the trajectory method. Finally I acknowledge with thanks the support of NSF Grant DMR87-03434 and ONR Grant N00014-84-K-0548.

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